INVESTIGATION OF LEACHING BEHAVIOUR OF PRE-CONCENTRATED COPPER ORE USING AMMONIUM CHLORIDE SOLUTION

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Abstract

Investigation of the leaching behaviour of near infrared sensor-based pre-concentrated and classified copper ore samples in ammonium chloride solution was studied to understand the trend in copper extraction. The mineralogical and chemical content of the ore was evaluated using QEMSCAN[®] and ICMP-MS techniques. The effects of leaching parameters such as NH₄Cl concentration, particle size, temperature, solid-to-liquid ratio and stirring speed on the leaching were determined. Results mineralogical analysis indicated that the copper bearing mineral in the ore is Chrysocolla with the product containing more copper content than the middling and waste. The middling ranked very high in hematite content than the other fractions while the waste contained significant quartz indicating higher gangue content than the product and middling. Copper extraction and elemental analysis of residue suggested that the rate of copper recovery in the product fraction was more significant than the middling which is in line with the mineralogical and NIR classification of the ore samples. The leaching parameters studied revealed that increasing temperature and NH₄Cl concentration with decreasing particle sizes and solid-to-liquid ratio led to increase in the rate of copper extraction up to 86.4 % and 67.3 % in the product and middling groups, respectively. Kinetic analysis revealed the activation energy to be 48.3 kJmol⁻¹ and 71.3k Jmol⁻¹, this suggests the dependence of the leaching process on surface chemical reaction.

KEYWORDS: *Pre-concentration, Sensor-based, Copper ore, Leaching, Ammonium chloride*

Introduction

Copper metal combines with a number of elements to form minerals containing carbonates, silicates, hydroxides, oxides, chlorides, sulphates, phosphates, and sulphides [1-2]. Copper is strategic metal, of the over two hundred minerals containing copper in discernible amounts, only a few are economically important [3]. High-grade ore resources of the copper metals in the world are in decline while the environmental cost and energy for processing of the lean mineral ores are increasing. With strong global demand for copper on the rise and the surge in prices of copper, there is the need for major mining companies to seek ways of processing low-grade and complex ores. Copper can be extracted either by smelting with refining, or by leaching, solvent extraction and electrowinning. The extraction process from sulphide ores is carried out to a large extent by pyrometallurgical processing techniques while the processing of oxide ores is enhanced by the hydrometallurgical technique. The decision whether to use pyrometallurgy or hydrometallurgy

is determined by balancing various social, environmental and economy considerations [3]. The continuous decline in copper has necessitated the quest for alternative ways of enhancing high copper recovery from low-grade ores. The emphasis has shifted to pre-concentration and energy-efficient metal extraction techniques for copper ores with high gangue content. Preconcentration of copper reduces downstream crushing and grinding requirements [4], as well as improving the leaching performance. The application of near infrared sensor-based method of copper ore pre-concentration, classification enhances leaching with high copper recovery from ores containing less than 1 % copper viable [5-9]. Furthermore, the recovery of copper traditionally involved pyrometallurgical treatment which, on account of emission of noxious flue gas and dust and production of slag waste, is increasingly substituted by hydrometallurgy [3, 9, 10,]. Sensor-base pre-concentration technology has a lot of potentials in the mining industry because it can be applied on relatively coarse ore particles; it is a valuable tool in mapping the

distribution of mineral alterations in hydrothermal ore deposits and in pre-concentrating porphyry Cu ore deposits [11-14]

In this study, copper ore has been preconcentrated using Near InfraRed Spectroscopy (NIR) according to the method described by [4]. this was undertaken to minimise high gangue content such as calcite. This was followed by crushing, grinding, and sieving of the preconcentrated ore according to ore grade based on two classifications (product and middling). Because the copper is finely disseminated in the ore, flotation is considered to be unsuitable and copper is leached from the size fractions instead [15]. Since acid leaching, forms a specific problem of high chemical consumption due to calcite hence the need to develop a process which leaches copper in an effective, fast and energy-efficient, comprehensive, easilycontrolled, and environmentally-safe manner. This is because factors which influence leaching performance are chemical composition and mineralogy of an ore, the type of leaching reagent, the temperature and pressure, the particle size distribution, the solid-liquid ratio, the rate of agitation, and the leaching period [16-18].

To avoid high acid consumption due to dissolution of calcite and other basic minerals during leaching, the applications of basic reagents to leach copper was considered effective [19-21]. Hence, we selected ammonium chloride as a reagent. It is well-known that ammonium chloride is able to dissolve copper oxide minerals and form stable copper-ammine complexes, promoting further dissolution of copper [22-25]. Other advantages of ammonium chloride as a reagent are its solubility in water and its lack of interaction with carbonates and siliceous gangue.

The shrinking core model was used to investigate the kinetics of the leaching process and mechanism controlling the reaction because the model is considered the best description of the heterogeneous reaction involving the conversion of copper particles and ammonium chloride during leaching [26-30]. The dissolution of metal is mainly controlled by factors such as degree of liberation, feed particle size, concentration of lixiviants and metal-bearing mineral grain [31].

Since the dissolution of copper occurs via different mechanisms, the objective of this work is to understand the leaching behaviour of a preconcentrated copper ore and determine the effect of sensor-base ore pre-concentration on leaching and the influence of experimental variables such as temperature, lixiviant concentration, stirring speed on the leaching process.

Experimental

Materials

The oxidised copper ore samples were obtained from a mine in northern Chile. Prior to the leaching studies samples were pre-concentrated using Near InfraRed Spectroscopy (NIR) sensorbased sorting technique and classified into product, middling and waste according to the method described by [4,32]. Only the product and middling fractions were advanced for leaching studies. All the chemicals used were analytical grade purchased from VWR International Ltd, UK. All solutions used were freshly prepared from analytical reagent grade chemicals and deionized water. The chemicals were used throughout the experiment without further purification. Work flow for the leaching strategy is shown in Fig.1.

Mineralogical analysis

The mineralogical analysis of the classified ore was carried out using a QEMSCAN[®] 4300 system, which is based on a Zeiss scanning electron microscope. The instrument is an automated technique for rapid mineralogical assessment, including the spatial mapping of minerals, via combined Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry (SEM-EDS).

Chemical analysis

Individual samples were separately crushed, ground, homogenize and sieved to different size fractions of -63+45 µm, -90+63 µm, and -125+90 µm. The chemical analysis of the different size fractions was carried out by dissolving the fractions in Aqua Regia (75 % conc. HCl, 25 % conc. HNO₃) and analysed with Inductively Coupled Plasma Spectrometry (ICP-Technology, MS. Agilent Model 7700). Experiments were mostly carried out with the -63+45 µm size fraction of the product and middling, unless otherwise stated.

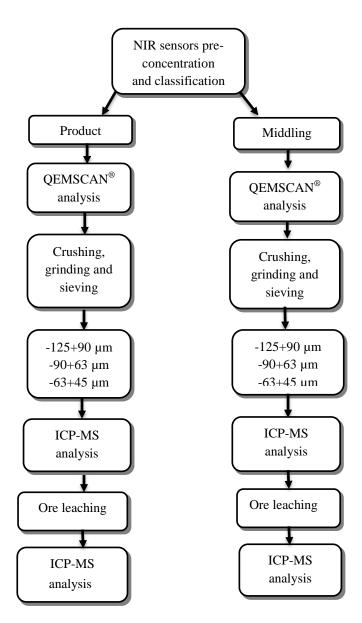


Fig.1: Work flow for leaching strategy

Leaching experiments

The leaching experiments were performed in a 500 mL reactor with a four-neck split flask in a heating mantle with thermostatically а temperature control unit. The reactor is equipped with an overhead mechanical stirrer and a rubber stopper to take samples from the leaching solution. The desired temperature for leaching was obtained by adjusting the thermostaticallycontrolled electric heating mantle. For each experimental run, 250 mL of freshly prepared aqueous NH₄Cl solution of predetermined molarity was charged to the reactor and heated to the required temperature before adding the solid

copper ore sample. After the desired stirring speed and reaction temperature were attained, 5 mL of leachate solution was withdrawn at time interval of 15 to120 minute, filtered using Whatman 540 filter paper and leachate determined for dissolved metals. The following experimental conditions: temperature 40 °C to 70 °C; ammonium chloride concentrations 0.5 M to 5.0 M; size fractions -63+45 µm; solid-to-liquid ratio 1/250, 2/250, 3/250 and 4/250 g/mL; stirring speed 300 rpm to 800 rpm and reaction time of 2h were maintained throughout the experiment unless otherwise stated. The fraction of the metal dissolved was calculated from the chemical composition of copper found (Table 2). Selected residue products obtained after 2 h leaching were oven-dried at 40 C for five days and analysed for metal contents using ICP-MS.

Results and Discussion

Mineralogical and chemical analysis of ore samples

QEMSCAN[®] mineralogical results shown in Table 1 indicated that the major copper-bearing mineral in the ore sample is chrysocolla (CuSiO₃. nH₂O). Other minerals containing copper (cuprite and malachite) were present at concentration well below 0.2%. Other mineralogical phases present in the ore include hematite, muscovite, biotite, kaolinite, chlorite, K- feldspar, Plagioclasefeldspar and quartz. The concentration of these minerals varied according to the ore category. The product fraction contained more copper, biotite and k-felspar than the middling and waste. The middling had more hematite content than the product and waste while the waste showed higher concentration of quarts signifying high gangue content than the product and middling. The ICP-MS chemical analysis for metals in the ore samples (Table 2) showed that the concentration of copper in the product is higher than that of the middling and waste. The concentrations of these selected metals (Zn, Mn, Co and Ni) were low compared to that of copper. This suggests good correlation for the sensor-base technique for the pre-concentration strategy. The mineralogical and chemical analysis revealed the chemical composition of the ore, which is key in evaluating the rate of copper extraction from the feed grade.

NIR Sampl e catego ry	Chrys ocolla	Hem atite	Cup rite	Musc ovite	Biot ite	Kaoli nite	Mala chite	Chl orite	Calci te	Anke rite	Quar tz	K- feldsp ar	Plagioc lase- feldspa r	Other s	Tota 1
Produ	3.93	23.92	0.01	2.89	10.9	0.11	0.17	11.6	2.87	0.50	14.1	27.23	0.25	1.41	100
cts					2			7			1				
Middl	2.70	48.75	0.00	3.20	4.98	0.54	0.00	6.63	1.73	0.69	15.2	14.11	0.39	1.05	100
ing											3				
Waste	0.73	1.47	0.02	4.06	7.38	0.01	0.17	20.6	12.10	0.64	34.0	15.63	0.84	2.21	100
								6			8				

Table 1: Mineralogical analysis of NIR sensor-based sorted ore samples with QEMSCAN[®], in wt-%

Table 2: Chemical composition of pre-concentrated ore fractions (-63+45 µm) with ICP-MS

Sample	Size	Cu (Wt-%)	Zn (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)
category	fractions					
Product	−63+45 µm	1.79	0.02	0.06	0.03	0.01
Middling	−63+45 µm	1.01	0.03	0.02	0.03	0.02

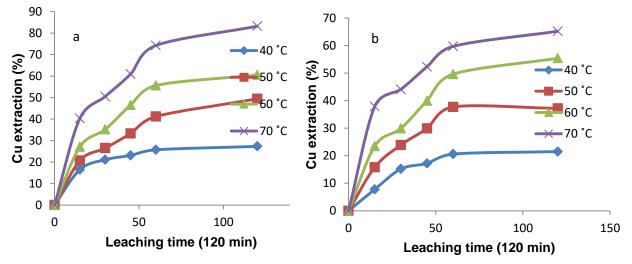


Fig. 2: Effect of temperature on pre-concentrated copper ore leaching: a (product), b (middling)

Effect of temperature

The effect of temperature on the leaching rate of the pre-concentrated ore was studied at temperature range of 40 to 70 °C. The following

parameters: 5.0 M NH₄Cl concentration, 1/250 g/mL solid-to-liquid ratio, $-63+45 \mu m$ size fractions and stirring speed of 300 rpm were kept constant throughout the experiment. The result of the effect of temperature is presented in Fig. 2 (a and b). It was found that increasing the

temperature of the reactant from 40 to 70 °C and leaching time of 2 h led to an increase in the rate of copper extraction from 21.5 % to 75% and 27.3 % to 89% in the middling and product ore fractions, respectively. The rate of copper dissolution is higher in the product when compared to middling. Expectedly, this is due to the difference in copper content (Tables 1 and 2) between the pre-concentrated ore. The observed

Kinetic analysis

The dissolution of copper in solution can be investigated using the shrinking core model [26, 33, 35]. The model was employed for kinetic investigation of the chemical leaching process in this work. The leaching process of the ore is described according to the expression in Equation 2:

A $(ANH_4Cl) + b$ (B solid Cu ore) \rightarrow NH₄Cl and /or solid copper product (1)

Where A and B is the solid-fluid reactant converted to $Cu(NH_3)_4^{2+}$ complexes /or solid copper product.

The shrinking of the ore particle is described using the kinetic models in Equations 2-4

increase in the rate of copper dissolution suggests the dependence of the leaching process on temperature. The enhancement of leaching by temperature is attributed to the fact that particles only react when there is effective collision between them. This is in conformity with [33, 34] on dependence of leaching on temperature.

$$1 - (1 - \alpha)^{1/3} = \frac{K_c M_B C_A t}{\rho s \beta r o} t = k_r t$$
⁽²⁾

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = \frac{2M_{S}DC_{A}t}{\rho_{S}\beta r^{2}o} = k_{d}t$$
(3)

$$\alpha = k_f t = \frac{3bk_c C_A}{\rho sro} \tag{4}$$

The leaching data obtained was tested according to the Equations 2-4 by plotting the fraction of copper reacted α , against time, *t*, for all the experimental data. Better fits were obtained with Equation 2 and was then applied for the kinetic analysis using the fraction of copper extracted in Fig. 2 (a and b). Results obtained indicated good agreement between the experimental results and the model (Equation 2). The rate constants, k_r were estimated from the slopes of the straight lines (Fig.3 (a and b).

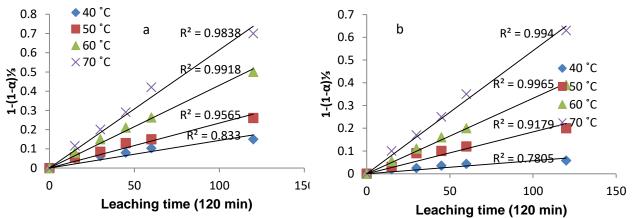


Fig. 3: Plots of $1 - (1 - \alpha)^{\frac{1}{2}}$ vs. time on pre-concentrated ore at various temperature: a (product), b (middling)

The temperature dependence of the chemical reaction between the reactants (NH_4Cl and copper ore particles) was estimated using the Arrhenius type relation in Equation 5:

$$k_r = A \exp\left[\frac{-Ea}{(RT)}\right] \tag{5}$$

Where A is the frequency factor and Ea is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. The activation energy was calculated from the apparent rate constants k_r obtained from slopes in Fig. 4a and b. The result of the plot $(\ln k_r)$ against the reciprocal of the temperature (1/T) is shown in Fig. 4(a and b). The activation energy calculated from the slopes of the Arrhenius relation in Fig. 4 is 48.3 kJ/mol and 71.3 kJ/mol for product and middling, respectively. This suggests that the rate of copper dissolution is controlled by surface chemical reaction. This is

in agreement with temperature sensitive leaching reactions by [34, 36-37]. The variation in activation energy in the pre-concentrated ore may be related to the mineralogical content of the ore. The middling with a value of 71.3 kJ/mol is greater than that of the product suggesting that more energy is needed to break the pore containing copper-bearing minerals for effective copper leaching. With stirring speed revealing weak effect on the dissolution of copper (Fig. 13) is a further proof that the leaching process is not diffusion controlled.

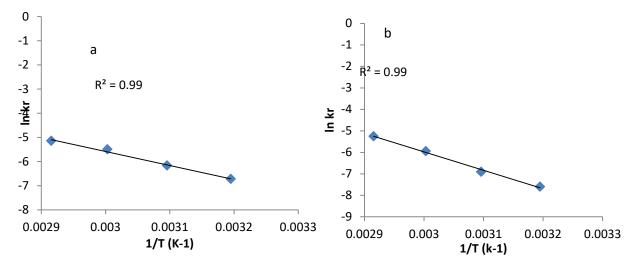


Fig.4: Arrhenius plots ln k vs 1/T for pre-concentrated ore: a (product),b (middling)

Effect of ammonium chloride concentration

The effect of NH₄Cl concentration on the extent of leaching of pre-concentrated ore was investigated using NH₄Cl concentrations of 0.5 to 5.0 mol.L⁻¹. During the experiment, solid-toliquid ratio of 1/250 g/mL, particle size of -63+45 µm, stirring speed of 300 rpm and reaction temperature of 70 °C were kept constant. The extent of copper dissolution increased considerably (Fig.5 (a and b) in both the product and middling with increase in NH₄Cl concentration. The leaching process is initiated by ionisation of NH₄Cl in aqueous medium and the hydrolysis of NH_4^+ which generates NH_3 ligand required for the reaction. The hydrolysis reaction leading to the formation of NH₃ is an important step, because it the driver in the reacting media and is said to occur according to the reaction in Equation 6:

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$
 (6)

The products formed in Equation 6 play important roles in the ore leaching process [32]. According to [16, 38], the formation of intermediate copper ammonia complexes species involving $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^{2+}$ species occurs during the ammoniacal leaching. The complexes are further converted to the stable $(Cu(NH_3)_4^{2+})$ [33]. The presence of these intermediate ligand species in the leaching media enhances the dissolution of more copper in the solution. The leaching rates recorded after 2 h were 65.0 and 83.3 % (middling and product) above which no further increase was obtained.

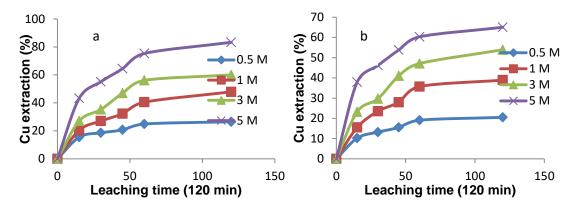


Fig.5: Effect of NH_4Cl concentration on leaching behaviour of pre-concentrated ore: a (product), b (middling)

Apparent rate constants of the reactions were determined from Fig. 5, for the various NH₄Cl concentrations by plotting $1 - (1-\alpha)^{\frac{1}{3}}$ vs. time, *t* (Fig.6 (a and b). The linear relationship between $1-(1-\alpha)^{\frac{1}{3}}$ and leaching time (*t*) further suggests that the dissolution process is controlled by chemical reaction at the interface .The reaction order with respect to NH₄Cl concentration was determined from the plot of ln kr vs. ln [NH₄Cl], Fig.7 (a and b) was obtained. From the tangent of the slopes the apparent reaction order for the dissolution of the ore by the alkaline reagent was estimated to be approximately equal to 1 in both

the middling and product. The kinetic equations relating to the effect of initial lixiviant concentration on the leaching rate are presented in Equations (7) and (8), respectively:

$$Lnkr = 0.43ln [NH_4Cl] - 6.7$$
(7)

 $Lnkr = 0.46 ln [NH_4Cl] - 7.8$ (8)

The apparent reaction order is an indication that the leaching reactions of the pre-concentrated ore samples with NH₄Cl are similar as indicated by the closeness in the values.

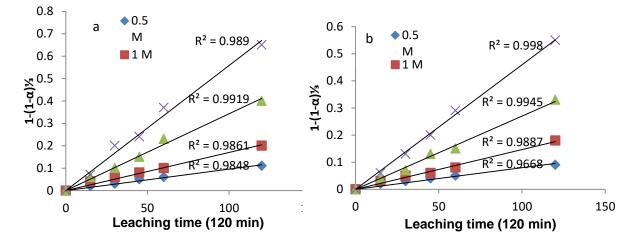


Fig.6: Plot of $1 - (1-a)^{\frac{1}{2}}$ vs. time on pre-concentrated ore at various NH₄Cl concentration: a (Product), b (middling)

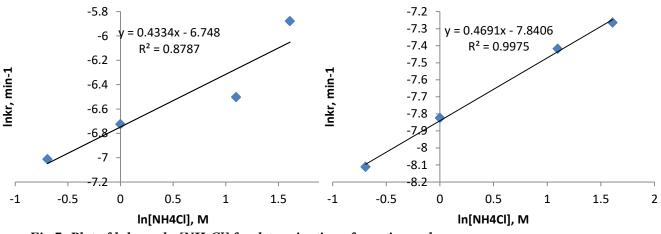


Fig.7: Plot of lnkr vs. ln [NH₄Cl] for determination of reaction order

Effect of particle size

Effect of different particle sizes on the leaching behaviour of the ore was determined using three different size fractions ($-63+45\mu$ m, $-90+63\mu$ m and $-125+90\mu$ m). Optimization of the effect of the particle size fractions was attained by keeping NH₄Cl concentration at 5.0 M, temperature at 70 °C, solid-to-liquid ratio at 1/250 g/mL and stirring speed constant at 300 rpm. The result of the effect of particle sizes is presented in Fig. 8 (a and b). It was found that the rate of leaching increased with a decrease in particle size fractions. About 85 % copper extraction was attained in the product and 68 % in the middling. Conversely, the $-63+45\mu$ m fraction led to greater copper extraction in both the samples due to increase in interfacial area. The smaller the diameter of a particle, the more it is amenable to leaching. This is due to high surface area to volume ratio available for contact with lixiviant. The result is an indication that finer size fraction enhances more copper dissolution, thereby allowing fast leaching kinetics. The observation of the dependence on effective leaching with decreasing size fraction is in line with [25-27, 34]. In order to establish the mechanism of the process, the dependence of the particle size on leaching was tested by determining the particle radius and values fitted into the kinetic models (Equations 2 to 4).

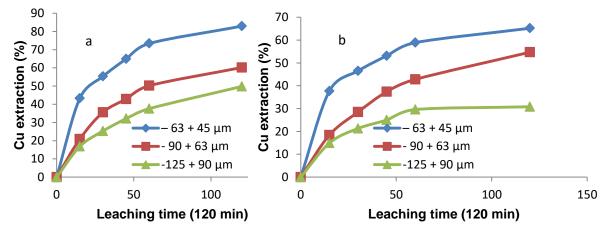


Fig.8: Effect of particle size on the leaching behaviour of pre-concentrated ore: a (product), b (middling)

The average particle radius was calculated using their geometric averages in Equation 9:

$$r_{0} = \sqrt{\frac{(F1F2)}{2}}$$
 (9)

The calculated values of the apparent rate constants kr obtained from the plot of $1 - (1-\alpha)^{\frac{1}{3}}$ vs. time for the three different particle sizes fractions were fitted (Fig. 9 (a and b), values obtained were then plotted against the inverse of initial particle radii shown in Fig. 10 (a and b). The plot indicated a linear dependence of the

rate constants on the inverse of the particle radius. With the line passing through the origin further suggests that the leaching process is controlled by chemical reaction. Thus, linearization of the kinetic data showed an increase in rate constant values with decreasing particle size. The closeness in \mathbb{R}^2 values for the classified ores is an indication that regardless of the variation in mineralogical content of the product and middling copper ore fractions, the leaching of copper from the ore increases with decreasing particle size fraction.

Effect of solid- to- liquid ratio

The effect of solid- to- liquid ratio on the leaching behaviour of the pre-concentrated ore investigated by keeping was NH₄Cl concentration, stirring speed, and particle size and reaction temperature constant. The leaching rate increases with decrease in solid-to-liquid ratio (Fig.11 (a and b). The solid-to-liquid ratio of 1/250 g/mL gave the highest copper dissolution and was considered for optimization of other experimental parameters. Different dissolution rates were obtained for the product and middling. The variations in leaching behaviour relates to the difference in the copper content in the pre-concentrated ore. When the data in Fig.11 (a and b) was fitted into the shrinking core model a positive correlation was obtained for the surface chemical reaction model in Equation 2. A plot of lnkr vs. ln [SL] (Fig.12) revealed the kinetic equations of the leaching (Eqs.10 and 11) with respect to solid-to-liquid ratio. The values are close to that obtained in Eqs.7 and 8 signifying a similar reaction process.

$$Lnkr = -0.48ln [SL] - 7.36$$
(10)

$$Lnkr = -0.71ln [SL] - 7.62$$
(11)

The little variation in the kinetic equation between the middling and product suggest the variation in mineral composition probably due to the difference in amount of gangue content between them. This is an indication that the mineral composition within the ore can be a major factor controlling the rate of copper dissolution.

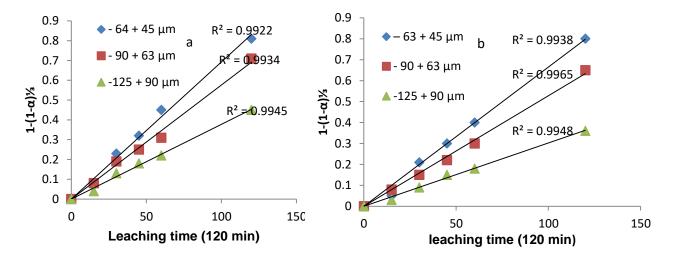


Fig. 9: Plots of $1 - (1-\alpha)^{1/3}$ vs. particle sizes: a (product), b (middling)

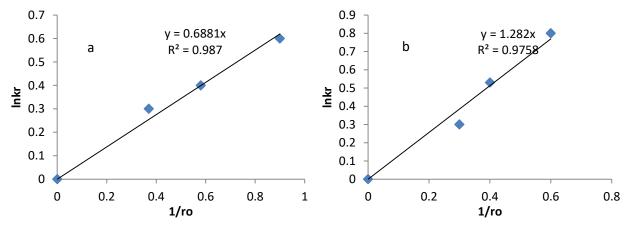


Fig. 10: Plot of apparent rate constant vs. inverse of particle radius: a (product), b (middling)

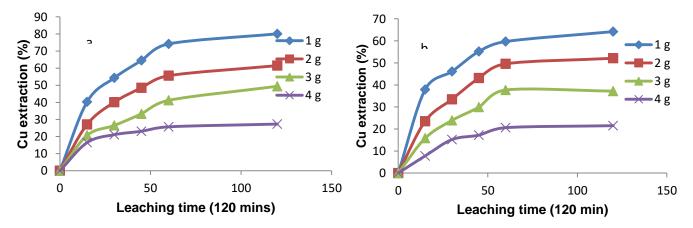


Fig.11: plot of $1 - (1-a)\frac{1}{3}$ vs. time for various solid-to-liquid ratio: a (product), b (middling)

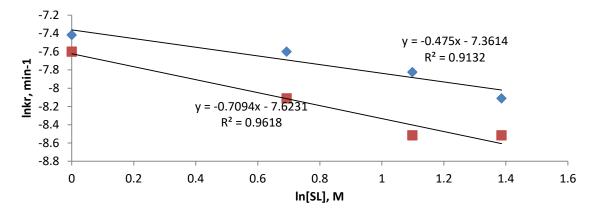


Fig.12: plot of lnkr vs. ln [SL] for determination of reaction order

Effect of stirring speed

The effect of stirring speed on the leaching behaviour was carried out to further establish the mechanism of the leaching process. The experiment was conducted using stirring speed of 300 to 800 rpm, in each case the stirring speed was varied while the other experimental variables were kept constant. Results of leaching revealed that agitation speed above 300 rpm led to a decrease in dissolution of copper. The rate of copper extraction decreased significantly from high values of 64 % and 83.5 % to low values of 40 % and 50 % (Fig. 13 (a and b) in the middling and product fractions, respectively. The higher extraction of copper at low stirring speed is as a result of effective collision between the leaching agent and the ore leading to significant dissolution compared to high stirring speed where less collision occurs. This is an indication that high stirring speed above 300 rpm is not required for the leaching of the ore. Optimal rate was obtained

at 300 rpm and was used for optimization of other parameters (temperature, solid-to-liquid ratio, particle size and ammonium chloride concentration) during the experiments. Plot of 1- $(1-\alpha)^{\frac{1}{3}}$ vs. time, t fitted well (Equation 3) when the experimental data were tested. The kinetic Equations about the stirring speed were determined from the rate constants of the values. The plot of lnkr vs. ln [SS] (Fig. 14), gave Eqs. (12) and (13) used to describe the kinetic equations on the effect of stirring speed on the leaching behaviour of the pre-concentrated ore.

$$Lnkr = -0.29 \ln [SS] - 5.5$$
 (12)

 $Lnkr = -0.57 \ln [SS] - 4.0$ (13)

The non-dependence of leaching on high stirring speed is an indication that excessive agitation above 300 rpm led to interruption of the leaching process. This suggests that the leaching process is chemically controlled.

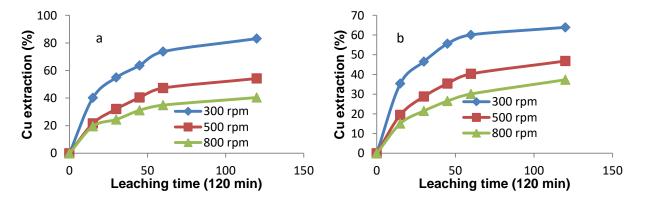


Fig.13: Effect of stirring speed on leaching behaviour of copper ore: a (product), b (middling)

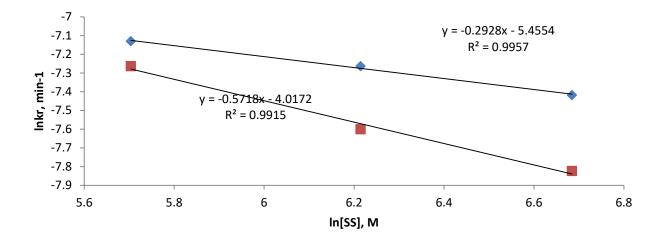


Fig. 14: plot of lnkr vs. ln[SS] for pre-concentrated ore: a (product), b(middling)

Elemental composition of ore residue

The ore residues obtained after optimal leaching from the feed grade in Table 2 was investigated for effectiveness of leaching after 2 h. Results of ICP-MS residue analysis is presented in Table 3. Comparison of the residue compositions with the feed grade revealed that most of the copper metal were leached substantially from the preconcentrated ore. The percentage copper recovery in the leach residue was calculated after [39] using the expression in Equation 14:

$$J(\%) = \frac{W_m \times Cu_a - W_r \times Cu_r}{W_m \times Cu_a} \times 100 \quad (14)$$

Table 3: Metal analysis of residue after 2 h leaching (%)

Metal→ Ore category↓	Cu (Wt- %)	Zn (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)
Product residue	0.17	0.01	0.04	0.01	0.00
Middling residue	0.13	0.01	0.01	0.01	0.01

With extraction rate above 80.4 % obtained in the product and 67.3 % in the middling from the feed grade, the remaining copper not leached (Table 3) may still exist in the inner core of the particle. These metals (Mn, Ni, Zn and Co) did not dissolve substantially in the solution when compared to the feed grade. However, most of the copper metal has been leached out of the preconcentrated ore by the reagent. The result of the extent of copper extraction was in accordance to the NIR sensor-based pre-concentration. This further suggests that the amount of copper dissolved from the ore varied with the ore classification. The observed copper leaching behaviour is an indication of the suitability of the NH_4Cl leaching process.

Conclusions

The leaching results indicated good correlation between QEMSCAN[®] mineralogical analysis and NIR sensor-based pre-concentration. The amount of copper extracted in the product and middling is in line with the NIR ore preconcentration. Kinetic equations for solid- toliquid ratio and stirring speed suggest slight variation in mineralogical composition of the ore matrix between middling and product samples. The leaching process is strongly influenced by temperature, particle sizes and ammonium chloride concentration. The kinetics analysis revealed that the leaching process is surface chemical controlled due to the independence of the process on stirring speed. The high values of activation energy above 12 kJ/mol suggest that the leaching process is chemically controlled. Variation in the extraction rate of copper between the product and middling is an indication of the variations in terms of amount of copper available for leaching. The near infrared pre-concentration led to improvement in copper extraction in the ores with NH₄Cl. This implied that ore processing options could be decided based on the amount of copper available for leaching and or gangue content. The result obtained outlines the potential of sensor-base technique in improving copper recovery during processing and alkaline leaching reagent in mitigating the problem of calcite consumption. Thus, the dissolution of other minerals into the leachate is minimised due the less aggressive nature of the reagent.

Nomenclature

A-Frequency factor in Arrhenius Equation;

b-Stoichiometric coefficient in Eq.(1);

C- Concentration of ammonium chloride reactant (mol/cm³);

Ea-Activation energy (J/ mol);

 f_1 , f_2 -Upper and lower sizes in a particular size fraction;

Kc-Liquid-solid mass transfer coefficient (m/s);

Kd-Apparent rate constant for product layer diffusion (s^{-1}) ;

Kr-Apparent rate constant for surface chemical reaction (s^{-1}) ;

Ks-Intrinsic reaction rate constant;

PS-Particle size and ρ_s Density of solid;

R-Universal gas constant (8.3145 J/(mol.k));

*r*0-Initial particle radius (m);

SL- Solid-to-liquid ratio;

SS -Stirring speed;

t-Time (h)

T-Temperature (K);

 α -Copper fraction extracted

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References

1. G. D. Zhao, H. S. Wu, Y. Zhang and Q. Liu (2004), Ammonia leaching of tailings from a copper mine, *Nonferrous Metals-Beijing*,**56**(3), 54-56.

2. G. D. Zhao, Q. Liuc (2010), Leaching of copper from tailings using ammonia/ammonium chloride solution and its dynamics, *Chemistry and Chemical Engineering International Conference*,216-220.

3. F. Habashi (1997), Handbook of Extractive Metallurgy, Volume 2. Wiley-Vch(1997).

4. S. Iyakwari, H. J. Glass, P. B. Kowalczuk (2013), Potential for near infrared sensor-based sorting of hydrothermally-formed minerals, *Journal of Near Infrared Spectroscopy*, **21**(3), 223-229.

5. J. E. Tilton (2003), On borrowed time? Assessing the threat of mineral depletion, Resources for the Future.

6. R. D. Simpson, M. A. Toman, R. U. Ayres (2012), Scarcity and Growth Revisited: Natural Resources and the Environment in the New MilleniumRoutledge.

7. S. H. Ju, M. T. Tang, S. H. Yang (2006), Thermodynamics and technology of extracting gold from low-grade gold ore in system of NH₄C1-NH₃-H₂O, *Transactions of Nonferrous metals society of China*, **16**(1), 203-208. 8. J. O. Marsden (2008), Energy efficiency and copper hydrometallurgy. *Hydrometallurgy*, 29-42.

9. Z. X. Liu, Z. L. Yin, H. P. Hu, Q. Y. Chen (2012), Leaching kinetics of low-grade copper ore with high-alkality gangues in ammoniaammonium sulphate solution, *Journal of Central South University of Technology*, **19**(1), 77.

11. J.D. Salter, N.P.G. Wyatt (1991), Sorting in the minerals industry: past, present and future. Miner. Eng. 4, 779–796.

12. H. Wotruba, M.R. Robben, D. Balthasar (2009), Near-infrared sensor-based sorting in theminerals industry. In Proc. Conference in minerals engineering. Lulea TechnicalUniversity, Lulea (Sweden), pp. 163– 176.

13. D. Pirrie, and G.K. Rollinson (2011), Unlocking the applications of automated mineral analysis. *Geology Today* **27**(6), 226-235.

14. M. Dalm, W.N.B. Michael, J.A. Frank, R Van, H.L.V. Jack (2014), Application of near infrared spectroscopy to sensor based sorting of porphyry copper ore, Minerals Engineering, 58: 7-16

15. I. A. Amos, A. B. Alafara, D. A. Bako, I. O. Janet, I. A. Kuranga (2017), Leaching kinetics of near infrared sensor-based pre-concentrated copper ores by sulphuric acid, *Physicochem. Probl.Miner. Process*, 53: 489–501.

16. P. G. Tzeferis and S. Agatzini-Leonardou (1994), Leaching of nickel and iron from Greek non-sulphide nickeliferous ores by organic acids, *Hydrometallurgy*,**36**(3), 345-360.

17. X. L. Sun, B. Z. Chen, X. Y. Yang, Y. Y. Liu (2009), Technological conditions and kinetics of leaching copper from complex copper oxide ore, *Journal of Central South University of Technology*, **16** (6), 936.

18. Y. Ghorbani, M. Becker, A. Mainza, J. P. Franzidis, J. Petersen (2011), Large particle effects in chemical/biochemical heap leach processes–A review, *Minerals Engineering*,**24** (11), 1172-1184.

19. T. Calban, S. Colak, M. Yeşilyurt (2005), Optimization of leaching of copper from oxidized copper ore in NH_3 - $(NH_4)_2SO_4$ medium, *Chemical Engineering Communications*, **192** (11), 1515-1524.

20. W. Liu, M. T. Tang, C. B. Tang, J. He, S. H. Yang, J. G. Yang (2010), Dissolution kinetics of low grade complex copper ore in ammoniaammonium chloride solution, *Transactions of the Nonferrous Metals Society of China*, **20** (5), 910-917.

21. A. Künkül, A. Gülezgin, N. Demirkiran (2013), Investigation of the use of ammonium acetate as an alternative lixiviant in the leaching of malachite ore, *Chemical Industry & Chemical Engineering Quarterly*, **19**(1), 25-34.

22. C. Ek, J. Frenay, J. C. Herman (1982), Oxidized copper phase precipitation in ammoniacal leaching—the influence of ammonium salt additions, *Hydrometallurgy*,**8** (1), 17-26.

23. J. E. Dutrizac (1992), The leaching of sulphide minerals in chloride media, *Hydrometallurgy*, **29** (1), 1-45.

24. F. A. Forward and E. Peters (1985), Leaching principles. SME Mineral Processing, Handbook, 2-13.

25. X. Wang, Q. Chen, H. Hu, Z. Yin, Z. Xiao (2009), Solubility prediction of malachite in aqueous ammoniacal ammonium chloride solutions at 25° C, *Hydrometallurgy*,**99**(3), 231-237.

26. F. Habashi (1980), Principles of Extractive Metallurgy, Second ed. Gordon & Breach, New, York.

27. H.S. Ray (1993), Kinetics of Metallurgical Reactions, Oxford and IBH Publishing, New Delhi.

28. S. Aydogan, A. Aras, M. (2005), Canbazoglu, Dissolution kinetics of sphalerite in acidic ferric chloride leaching, *Chemical Engineering Journal*, **114**(1), 67-72.

29. S. A. Awe, Å. Sandström, (2010), Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution, *Minerals Engineering*, **23**(15), 1227-1236.

30. A. A. Baba, M. K. Ghosh, S. R. Pradhan, D. S. Rao, A. Baral, F. A. Adekola (2014), characterization and kinetic study on ammonia leaching of complex copper ore, *Transactions of*

Nonferrous Metals Society of China, **24**(5), 1587-1595.

31. N. Habbache, N. Alane, S. Djerad, L. Tifouti (2009), Leaching of copper oxide with different acid solutions, *Chemical Engineering Journal*, **152**(2), 503-508.

32. S. Iyakwari, H. J. Glass, G. K. Rollinson, P. B. Kowalczuk (2016), Application of near infrared sensors to preconcentration of hydrothermally-formed copper ore, *Minerals Engineering*, 85: 148-167.

33. O. Levenspiel (1999), Chemical reaction engineering, *Industrial & Engineering Chemistry Research*, **38**(11), 4140-4143.

34. F. Parada, M. I. Jeffrey, E. Asselin (2014), Leaching kinetics of enargite in alkaline sodium sulphide solutions, *Hydrometallurgy*, 146: 48-58.

35. A. Ekmekyapar, N. Demirkiran, A. Künkül (2008), Dissolution kinetics of ulexite in acetic acid solutions, *Chemical Engineering Research and Design*,**86**(9), 1011-1016.

36. A. Ekmekyapar, E. Aktaş, A. Künkül, N. Demirkiran (2012), Investigation of leaching kinetics of copper from malachite ore in ammonium nitrate solutions, *Metallurgical and Materials Transactions B*,**43**(4), 764-772.

37. A. Darchen, R. Drissi-daoudi, A. Irzho (1997), Electrochemical investigations of copper etching by Cu (NH3) 4Cl2 in ammoniacal solutions, *Journal of Applied Electrochemistry*, **27**(4), 448-454.

38. D. Bingol, M. Canbazoglu, S. Aydogan (2005), Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching, *Hydrometallurgy*,**76** (1) 55-62.

39. J. Liu, S. Wen, D. Liu, M. Lv, and L. Liu (2011), Response surface methodology for optimization of copper leaching from a low-grade flotation middling. *Minerals and Metallurgical Processing*, **28** (3), 139